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Levels of Benzo(a)pyrene in Oil Shale Industry Wastes, Some Bodies of Water in the Estonian S.S.R. and in Water Organisms

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Data on the content of benzo(a)pyrene (BP) in oil shale industry wastewater, the effectiveness of various effluent treatment processes (evaporation, extraction with butyl acetate, trickling filters, aeration tanks) in reducing the level of BP in oil shale wastewater, the level of BP in various bodies of water of Estonia, and in fish and other water organisms are reviewed.

The quantitative determination of BP in concentrated diethyl ether extracts of water samples was carried out by ultraviolet and spectroluminescence procedures by use of the quasi-linear spectra at −196°C in solid paraffins. It has been found that oil shale industry wastewater contains large amounts of BP. The most efficient purification process for removing the BP in oil shale industry phenol water is extraction with butyl acetate.

The level of BP in the rivers of the oil shale industry area is comparatively higher than in other bodies of water of the Republic. The concentration of BP in the lakes of the Estonian S.S.R. is on the whole insignificant. Even the maximum concentration found in our lakes is as a rule less than the safety limit for BP in bodies of water (0.005 μg/l.). Drinking water is treated at the waterworks. The effectiveness of the water treatment in reducing the level of BP varies from 11 to 88%. Filtration was found to be the most effective treatment.

About 200 samples of fish from nine bodies of water in Estonia have been analyzed for content of BP. The average content of BP in the muscular tissue of various species of fish is as a rule less than 1 μg/kg. There is no significant difference in the concentration of BP in sea and freshwater fish. There is no important difference in the content of BP in the organs of various fish. Fat fish contain more BP than lean ones. The weight (age) of fish does not influence the content of BP in the muscular tissue of fish.

Numerous data on levels of benzo(a)pyrene (BP) and other polycyclic hydrocarbons (PAH) in various water bodies have been published (*1–3*). The principal sources of PAH in water are industrial sewage, smoke, and other emissions as well as automobile exhausts.

The products of oil shale processing (various shale oils) contain about 0.002–0.17% BP. Since 1972 we have studied the concentration of BP in sewage of the oil shale industry, as well as the effectiveness of different sewage treatment processes and the levels of BP in bodies of water. The rivers of the oil shale region of Estonia and the water reservoir of Narva as well as the River Plyussa which feeds into the Narva Reservoir have been investigated. The studies were expanded also to other bodies of water of the Estonian S.S.R., especially to some major lakes. Water samples (1–3 liters) from different departments of the oil shale plant and from various bodies of water were repeatedly extracted with diethyl ether or benzene. The extracts were concentrated. The quantitative determination of BP was carried out by ultraviolet and spectroluminescence procedures by a modification of the method of Khesina (*3*) by using the quasilinear spectra at −196°C in solid paraffins.

Investigations on bodies of water were carried out every season during a two-year period. Samples were taken at fixed points in all cases.

The data on levels of BP in oil shale industry wastewater (Table 1) confirm that the greatest

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amounts of BP are found in wastes from the chamber oven (high-temperature process) department. The phenol-containing wastewater of the Kohtla-Järve Integrated Plant contains quantities of BP which are about twelve times those from comparable phenol-containing wastewater from the Kiviöli Plant. This is explained by the absence of high-temperature chamber ovens at the latter.

To evaluate the efficiency of different effluent treatment processes (evaporation, extraction with butyl acetate, trickling filters, aeration tanks) in reducing the level of BP in oil shale wastewaters, samples of water were taken before and after every treatment process (Table 2).

Some samples of butyl acetate and of the crude phenol extract were also analyzed. Extraction of phenols with butyl acetate was found to be the most efficient process for purification of wastewater with respect to BP, its concentration being reduced by the treatment process about 12-34 times. Butyl acetate does not contain BP; it concentrates in the extract of crude phenols.

The crude phenol extract is used as the main component in producing synthetic tanning substances. As most of the BP remains in the phenol extract, preventive measures were proposed for working with phenol extracts as well.

The evaporation method which was used for the treatment of phenol wastes at the Kiviöli Plant in the period 1959–1964 was less effective than the extraction with butyl acetate: the concentration of BP was reduced as a result of evaporation only about 2-2.5 times.

At the Kohtla-Järve Plant the wastes are mixed after dephenolization with wastewater containing small quantities of phenols and with the communal sewage. The mixed effluents are treated by passage through trickling filters. The removal of BP is not high (Table 2). The activated sludge process in the aero-tanks of the Slantsy Oil Shale Integrated Plant is more effective than trickling filters.

Rivers into which the wastewaters of oil shale industry of Estonia are released, contain higher levels of BP than other water bodies of the Republic. The data on the Narva Reservoir are presented in Table 3.

Analyses from the Narva Reservoir in various seasons have shown the highest BP values in summer and winter. During spring highwater and autumn rains the BP concentration was about 5-6 times smaller. In the sand taken from the ground of the water reservoir, BP was found in concentrations from 3.86 to 19.8 μg/kg.

The comparison of our data on the amount of BP in the Narva Reservoir with the results of Dikun and Makhinenko (*4*) is of great interest. They studied the level of BP in the Narva Reservoir and the River Plyussa in 1963 (*4*) and found the concentration of BP to be approximately 1 μg/l. Our data, obtained about 10 years later, showed a level of BP which was almost a thousand times lower. This is apparently due to the efficiency of the wastewater treatment measures put into practice at the Slantsy Oil Shale Integrated Plant.

Estonia is rich in lakes; there are approximately 1500 of them. Analyses of BP were carried out in a number of them, taking into consideration their hydrobiological characteristics and economic importance.

Many of our lakes are popular as places for rest and recreation, for example Lakes Pikkjärv, Linajärv, Kuremaa, and Saadjärv. Lake Ülemiste is the main drinking water supply for our capital, Tallinn. Hydrobiological investigations have shown that

Table 1. Concentration of BP in the wastewater from the oil shale industry.

Source	Concentration of BP, mg/l.
Kohtla-Järve Integrated Plant	
General effluent	0.02–0.068
Phenol water from the chamber-oven department	0.14–0.16
Phenol water from the tunnel-oven department	0.015–0.027
Phenol water from the generator department	0.04–0.05
Total effluent from the Kiviöli Integrated Plant	0.0015–0.005

Table 2. Reduction of BP by industrial effluent treatment processes.

Source of BP	Concentration of BP, mg/l. Kohtla-Järve Plant	Concentration of BP, mg/l. Kiviöli Plant
Water before dephenolization	0.02–0.068	0.0015–0.005
Water after dephenolization	0.0016–0.002	0.0008–0.002
Butyl acetate	0	—
Extract of crude phenols	11.8–13.5	—
Water before trickling filters	0.00016	—
Water after trickling filters	0.00012	—

Table 3. Concentration of BP in the Narva Reservoir.

Source	BP, μg/l.
By the ash pond of the Baltic power station	0.0045
From the canal of the Baltic power station	0.0016
From the new water supply of Narva	0.0044
From the canal of the Estonian power station	0.0015
From the waterworks of Narva (drinking water) (near Kulgu Harbor)	0.005

most of our lakes must be qualified as eutrophic.

The average concentrations of BP in the most important investigated lakes are presented in Table 4.

Data presented in Table 4 permit us to draw the conclusion that the quantities of BP in our lakes are relatively small. The level of BP is often smaller than in such nonpolluted lakes as the Bodensee where Borneff and Kunte (*5*) found 0.0013 μg/l. BP. Even the maximum concentrations found in our lakes do not reach the safety limit for BP in water bodies, which is equal to 0.005 μg/l.

The seasons have no influence on the level of BP in the lakewater, as can be seen in Table 5. Perhaps this can be explained by the relative stability of their hydrological regimen.

On evaluating the data of our studies in comparison with the data of Ilnitski et al. (*6*), we noted similar fluctuations of the concentration of BP in the water bodies of Estonia as in other water bodies of the Soviet Union. In general, the BP levels in water are insignificant compared with those in food. Besides, surface water is treated before it is used for drinking.

We were interested in the effectiveness of water treatment at the Estonian water treatment plant. Studies were carried out in Narva. It was found that the effectiveness of the water treatment at the waterworks of Narva varied from 11 to 88%. Similar data (11–85%) were reported by Ilnitski et al. (*6*).

A more detailed study was carried out at the Tallinn water treatment plant, where the effect of the drinking water treatment was investigated at different stages: after chlorination, after coagulation, and after filtration. Chlorination reduced the concentration of BP by about 20%; the coagulation process showed no influence. Filtration was found to be the most effective treatment as, it reduced the quantity of BP by approximately 50%.

Table 4. Concentration of BP in lake water.

Lake	BP, μg/l.
Ülemiste	0.0005
Pikkjärv	0.0009
Linajärv	0.0008
Kehala	0.0003
Karjatse	0.0004
Möldri	0.0005
Harku	0.0016
Kuremaa	0.0009
Kaiavere	0.0008
Kaarepere Pikkjärv	0.0020
Saadjärv	0.0003

The results of our study permit us to conclude that the level of BP in about 60 bodies of water in nonindustrial regions is many times lower than the safety limit for BP in such bodies, which is equal to 0.005 μg/l.

Many scientists (*7–12*) have mentioned that BP can be concentrated in various water organisms including fish. Estonians eat about 27 kg fish per capita per year; the average for the Soviet Union is 13.2 kg (*13*). Therefore, the BP content of the fish caught in Estonian waters is of great interest.

We have studied about 200 samples of fish from nine bodies of water in Estonia. The samples of fish were analyzed by the method of Dikun (*4*) for BP and by a modification of a method which permits one to determine the content of organochlorine pesticides and PAH simultaneously. These compounds were extracted from water with ether. In the dry residue the organochlorine pesticides were determined by gas chromatography. The content of BP was determined by employing the spectral luminescence method. The results of both the method of Dikun and the modified method were similar.

Table 6 presents data on the level of BP in fish filet tissue. The average concentrations fluctuate from 0.11 to 6 μg/kg. In most of the samples the BP level was less than 1 μg/kg. Exceptions containing more BP among sea fish were baltic herring and pike perch and among freshwater fish, salmon, eel, and bream.

It has been found that BP concentrates in various water organisms, especially in the food of fish. Most species of fish are nonpredatory; i.e., their food is mainly zooplankton. The predatory fishes feed on smaller fish. The average content of BP in zooplankton in our samples (Table 10) was 1.11 μg/kg (from 0.26 to 5.10 μg/kg). As the predatory fish eat fish which eat the plankton, we supposed that we would find more BP in the former. The results of our investigations (Table 7) did not support this presupposition.

We were also interested in determining the distribution of BP in various organs of fish. The results of our analyses are presented in Tables 8 and 9,

Table 5. Concentration of BP in lake water in various seasons.

Lake	BP concentration, μg/l.			
	Winter	Spring	Summer	Autumn
Ülemiste	0–0.0041	0–0.011	0.0002–0.0006	0.00035–0.0008
Linajärv	0–0.0005	0–0.0056	0.0005–0.0060	0.0005–0.0019

Table 6. Content of BP in the muscular tissue of fish.

Source	Species of fish	Number of samples	BP concentration, μg/kg		
			Minimum	Maximum	Average
Rivers of North Estonia	Trout	4	0.00	1.72	0.685
	Minnow	2	0.17	0.19	0.180
	Salmon	2	0.11	11.82	5.960
Various lakes	Tench	8	0.09	2.94	0.962
	Pike	11	0.05	0.41	0.187
	Eel	6	0.00	3.50	1.100
	Perch	8	0.02	1.90	0.835
	Roach	6	0.03	3.04	0.733
	Bream	32	0.00	10.00	1.694
	Pike-perch	4	0.23	0.76	0.417
Bays and gulfs	Baltic Sprat	23	0.22	4.48	0.99
	Baltic Herring	12	0.08	3.10	1.22
	Pike-perch	9	0.06	8.50	2.25
	Perch	2	0.10	0.52	0.31
	Silver bream	2	0.08	0.13	0.11
	White bream	2	0.20	0.48	0.34

Table 7. Level of BP in predatory and nonpredatory fish.

Fish	Number of samples	BP concentration, μg/kg		
		Minimum	Maximum	Average
Predators				
Pike	11	0.05	0.41	0.187
Pike-perch	4	0.23	0.76	0.417
Trout	4	0.00	1.72	0.685
Nonpredators				
Bream	32	0.00	10.00	1.694
Tench	8	0.09	2.94	0.962
Roach	6	0.03	3.04	0.733

which show that the concentration of BP fluctuates widely and there are no significant differences in the BP level of the liver, gills, hard roe, and milt.

We have tried to find out if there is any difference in the level of BP in the fish of various weights (ages). The data presented in Figure 1 show that the weight of the fish does not influence the BP content. A 1000 g fish contains the same concentrations of BP on the average as a 100-300 g specimen. Some metabolic processes may take place in the fish. L. Baranova et al. (*14*) fed trout and carp food containing BP. They found that if the total dose of BP in the food of a fish was about 12,600 μg/kg, the tissue of trout did not contain BP at all.

It is well known that organochlorine pesticides

Table 8. Comparative content of BP in various fish organs.

Fish	Organ	Number of samples	BP concentration, μg/kg		
			Minimum	Maximum	Average
Tench	Liver	2	0.15	0.78	0.47
	Roe	2	0.53	1.41	0.97
	Gills	2	0.16	0.17	0.16
Pike	Liver	8	0.20	1.45	0.75
	Gills	2	0.12	0.18	0.15
Bream	Liver	5	0.32	1.12	0.59
	Roe	1			0.08
	Gills	3	0.27	1.80	0.82
Baltic herring	Liver	6	0.39	5.24	1.69
	Roe	7	0.12	2.75	1.13
	Milt	11	0.17	0.91	0.46
	Gills	6	0.24	1.18	0.44

Table 9. Content of BP in the liver of various fish.

Fish	Number of samples	BP concentration, μg/kg		
		Minimum	Maximum	Average
Tench	2	0.15	0.78	0.47
Pike	8	0.20	1.45	0.75
Eel	3	0.26	4.20	2.02
Bream	5	0.32	1.12	0.59
Pike-perch	9	0.11	2.76	0.53
Baltic herring	6	0.39	5.24	1.69
Burbot	5	0.13	2.14	0.58

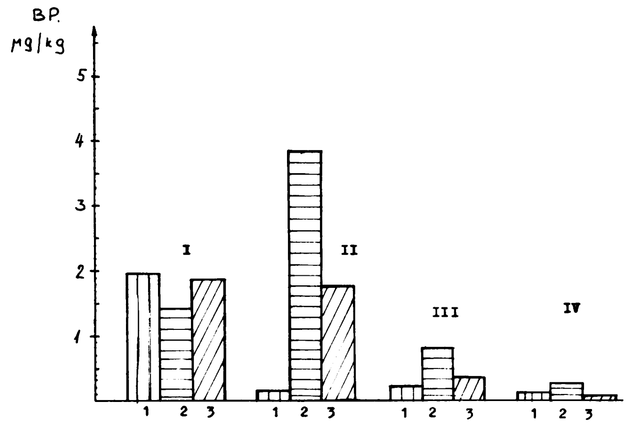

FIGURE 1. BP level in fish as a function of weight for (I) bream, (II) pike perch from sea, (III) pike perch from lakes, and (IV) pike: (1) 800-1100 g; (2) 400-600 g; (3) 100-300 g.

concentrate in the fat tissues. Therefore we intended to find out how BP behaves. By comparing the content of BP in fat and lean fish, we could establish that fat fishes (salmon, eel) contain more BP than the lean ones (pike, perch a. others).

It is of considerable importance to know how BP is distributed in water and various water organisms. As is shown in Table 10, BP seems to concentrate in the bottom sediments (sand), in algae and water plants as well as in the zooplankton. The concentration of that carcinogen in these objects is evidently higher than in fish.

The analyses of BP in water plants of some lakes showed (Table 11) that BP concentrates to a considerable degree in reed and duckweed.

Conclusions

Oil shale industry wastes contain large quantities of BP. The greatest amounts are found in the wastewater from the chamber oven. Dephenolation with butyl acetate is the most efficient purification process for BP in shale oil industry phenol wastewater.

The content of BP in the Narva Reservoir has decreased considerably during the last 10 years. The average amount of BP is now less than the safety limit for bodies of water. The concentration of BP in the lakes of the Estonian S.S.R. is on the whole insignificant. Even the maximum concentration found in our lakes is as a rule less than the safety limit for BP (0.005 μg/l.). The efficiency of water treatment in reducing the level of BP varies from 11 to 88%. Filtration is the most effective treatment.

Table 10. Level of BP in water, sediments and water organisms.

Source	Sample	Number of samples	Concentration, μg/kg or μg/l.		
			Minimum	Maximum	Average
Sea	Water	29	0.0000	0.0123	0.0007
bay	Sand (bottom sediments)	16	0.24	11.50	2.57
	Algae	2	2.40	3.00	2.70
	Zooplankton	13	0.26	5.10	1.11
	Baltic sprat	23	0.22	4.48	0.99
	Baltic herring	12	0.08	3.10	1.22
	Pike-perch	9	0.06	8.50	2.25
Lake	Water	32	0.0000	0.0047	0.0006
	Sand (bottom sediments)	2	2.10	4.30	3.20
	Water plants	10	1.32	129.0	36.9
	Roach	6	0.03	3.04	0.73
	Perch	8	0.02	1.90	0.83

Table 11. Content of BP in water plants.

Sample	Source	Number of samples	Concentration µg/kg of dry sample Minimum	Maximum	Average
Reed	Lake Harku	10	1.32	129.0	36.9
Duckweed	Lake Kahala	3	19.10	112.4	52.4
Reed	Lake Pikkjäru	5	3.36	51.6	14.8

The average content of BP in the muscular tissue of various species of fish, is as a rule less than 1 µg/kg. There is no significant difference in the concentration of BP in sea and fresh water fish. The content of BP in the muscular tissue of fish is independent of food. There is no important difference in the content of BP in the organs of various fish. Fat fish contain more BP than the lean ones. The weight (age) of fish does not influence the content of BP in the muscular tissue of fish.

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